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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

a. AD-A241 342 		1b. RESTRICTIVE MARKINGS													
b.		3. DISTRIBUTION / AVAILABILITY OF REPORT approved for public release; distribution unlimited													
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report No. 4		5. MONITORING ORGANIZATION REPORT NUMBER(S)													
5a. NAME OF PERFORMING ORGANIZATION The Pennsylvania State Univ.	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research													
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, 152 Davey Lab. University Park, Pennsylvania 16802		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217													
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER													
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO. N00014-91</td><td>PROJECT NO. J-1194</td><td>TASK NO. 4132007-06</td><td>WORK UNIT ACCESSION NO.</td></tr></table>		PROGRAM ELEMENT NO. N00014-91	PROJECT NO. J-1194	TASK NO. 4132007-06	WORK UNIT ACCESSION NO.								
PROGRAM ELEMENT NO. N00014-91	PROJECT NO. J-1194	TASK NO. 4132007-06	WORK UNIT ACCESSION NO.												
11. TITLE (Include Security Classification) Characterization and Conductivities of Polyphosphazene-Iodine Complexes															
12. PERSONAL AUTHOR(S) M. M. Lerner, A. L. Tipton and D. E. Shriver* (at Northwestern), A. A. Dembek and H. R. Allcock*															
13a. TYPE OF REPORT Reprint	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT												
16. SUPPLEMENTARY NOTATION Prepared for publication in CHEMISTRY OF MATERIALS															
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB-GROUP</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB-GROUP										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Polymers, phosphazenes, solid ionic conductivity, electroactive materials, batteries, MEEP	
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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> OTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynn		22b. TELEPHONE (Include Area Code) 703-696-4315	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1194
R&T Code 4132007-06

Technical Report No. 4

CHARACTERIZATION AND CONDUCTIVITIES OF POLYPHOSPHAZENE-IODINE COMPLEXES

by

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Prepared for Publication in CHEMISTRY OF MATERIALS

October 2, 1991

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Characterization and Conductivities of Polyphosphazene-Iodine Complexes

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Abstract

Complexes of phosphazenes with I_2 have been prepared with molecular and polymeric phosphazene/ I_2 ratios ranging from 8 to 0.2. For brevity the phosphazenes are identified as follows: $[NPCl_2]_n$; $[NP(OPr)_2]_n$ ($=[NP(OCH_2CH_2CH_3)_2]_n$), $[NP(OCH_2CF_3)_2]_n$ ($=NP(OTFE)_2$) $_n$ and $[NP(OC_2H_4OC_2H_4OCH_3)_2]_n$ ($=MEEP$). Resonance Raman spectra indicate that polyiodides are formed for all but the $[NPCl_2]_n$ -iodine system. Impedance measurements demonstrate high bulk conductivities near ambient temperature for the MEEP and $[NP(OPr)_2]_n$ -based systems. For all systems, the conductivity increases with increasing iodine loading.

Introduction

The preparation of ionically conducting solids is of broad fundamental interest. These materials have applications in solid-state electrochemical devices.^{1,2} Polymer-based complexes possess several advantages over semi-crystalline solids, and these advantages include ease of chemical modification and processability. Recent work has shown that high bulk conductivities at ambient temperature can be obtained for etheric polymer complexes that contain polyiodides.^{3,4}

Iodine forms charge-transfer complexes with a wide variety of polymers, or it may disproportionate to form polyiodides.⁵ Also, conjugated polymers such as polyacetylene become electronically conducting following reaction with many oxidizing agents, including I_2 .⁶ However, a number of monomers and non-conjugated polymers also form stable, highly conductive complexes with iodine. Examples include poly(vinylpyridine)⁷ and poly(alkylsulfides).⁸ The mode of conduction in iodine-doped poly(isoprene) has also been examined by several groups.⁹⁻¹¹

The poly(organophosphazene) $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (MEEP) was first synthesized and studied in our laboratories as a solid solvent for Li or Ag triflate salts. The solid solutions generated ionic conductivities that were several orders of magnitude higher than those of poly(ethylene oxide).¹²⁻¹⁶

Subsequent investigation of the conductivities of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_nMI_x$ (MEEP_nMI_x; M = Na, Li) complexes has led to the discovery of a number of stable MEEP-iodine complexes, MEEP_xI, which are free of alkali metal salt.³ At iodine loadings of $NP/I < 4$, the MEEP_nI complexes exhibit conductivities near 10^{-3} Scm^{-1} at ambient temperature. Polyiodides are clearly present in these

complexes; the formation of I_x^- from I_2 must therefore be balanced by a compensating oxidation reaction. The nature of this oxidation half-reaction is uncertain, but it seems probable that iodonium cations are formed by I^+ coordination to the oligoether side-chains of MEEP.

The primary aim of the present research was to survey the interaction of I_2 with a series of polyphosphazenes and thereby explore the chemical generality of I_2 disproportionation in molecular and polymeric phosphazene systems.

Experimental Section

The polyphosphazene polymers $[NP(OPr)_2]_n$, $[NP(OTFE)_2]_n$, and MEEP were prepared by established methods,¹⁷⁻¹⁹ and were purified by successive reprecipitations or dialysis, as appropriate. Residual water was removed by long-term evacuation. Weighed quantities of I_2 (Aldrich chemicals, reagent grade, resublimed prior to use) were allowed to diffuse as the vapor into weighed samples of the solid polyphosphazenes in air-tight glass cells at 60°C. The reactions were allowed to proceed for several days until neither solid nor gaseous I_2 remained and the complexes were homogeneous in appearance.

Resonance Raman spectra were collected at ambient temperature between 80 and 250 cm^{-1} on a SPEX 1401 monochromator using a 180° backscattering geometry and a Kr^+ (647 nm) excitation line. The solid samples were loaded under an inert atmosphere into 5-mm Pyrex tubes which were spun during data collection to minimize local heating. Differential scanning calorimetry (DSC) measurements were performed as described previously.²⁰ Samples were loaded under an inert atmosphere into hermetically-sealed aluminum pans. The results were consistent throughout several quenching and heating cycles indicating that loss of iodine from the sample was not a problem. NMR spectra

(^{31}P and ^{13}C) were recorded on a JEOL FX spectrometer (FT, 270 MHz) or a Varian spectrometer (FT, 400 MHz). Spectra were recorded in CDCl_3 or acetone- d_6 and referenced to the solvent. Chemical shifts (δ/ppm) are referenced to external 85% H_3PO_4 for ^{31}P NMR; upfield chemical shifts are negative.

AC impedance data were acquired from 10°C to 70°C over a frequency range of 10 MHz to 5 MHz using a Hewlett-Packard 4192 LF impedance analyzer for high-frequency and a Solartron Instruments 150 FRA for low-frequency measurements, both under computer control. The sample disks (ca. 1 mm) were pressed between tantalum (blocking) electrodes each 1/2 in. in diameter within an air-tight cell.

Results.

The products obtained by the interaction of polyphosphazenes with iodine are described in Table 1. In almost all cases, no residual solid or gaseous I_2 remained and the resulting complex was homogenous in appearance. However, as indicated in Table 1, high concentrations of iodine in $[\text{NP}(\text{Cl}_2)]_n$ resulted in systems in which unreacted solid I_2 remained after several days. The products obtained for all stoichiometries prepared with MEEP_xI and $[\text{NP}(\text{OPr})_2]_x\text{I}$ were brown-black. The mobility of the polymers decreased with increasing iodine content. The $[\text{NP}(\text{OTFE})_2]_x\text{I}$ complexes were brown and fibrous with morphologies similar to that of the pristine polymer. The addition of iodine to $[\text{NP}(\text{Cl}_2)]_n$ resulted in the formation of deep purple, rubbery complexes. The $[\text{NP}(\text{Cl}_2)]_x\text{I}$ complexes evolved I_2 rapidly when evacuated. When exposed to an inert atmosphere they lost coloration slowly until only a faint purple or pink hue remained. All other complexes were stable under an inert atmosphere.

Resonance Raman spectra of $[\text{NP}(\text{OPr})_2]_x\text{I}$ and MEEP_xI show characteristic

features of polyiodide anions. Peaks in the $109\text{--}113\text{ cm}^{-1}$ range are assigned to the symmetric stretching mode of an I_3^- species, while peaks near 170 cm^{-1} are assigned to higher polyiodides. The shoulder or small peak at ca. 145 cm^{-1} in every spectrum is assigned to the asymmetric stretching mode of an I_3^- species. All of these bands were absent in the spectrum of $[\text{NP}(\text{Cl}_2)]_x$ iodine mixtures because I_2 volatilized from the polymer and recrystallized in the sample tube. Some iodine loss was also observed for the I_2 doped samples of $[\text{NP}(\text{OTFE})_2]_4$ and $[\text{NP}(\text{OTFE})_2]_2$ samples. For these complexes, however, the polyiodide bands near 110 and 170 cm^{-1} were recorded along with a sharp band at 216 cm^{-1} ascribed to I_2 vapor.²¹

DSC traces (Table 3) obtained for both $[\text{NP}(\text{OPr})_2]_x\text{I}$ and MEEP_xI complexes reveal an increase in glass transition temperature (T_g) and a broadening of the transition as the iodine content increased. A strong endotherm was detected for $[\text{NP}(\text{OTFE})_2]_n$ at 310K , which corresponds to the melting of a crystalline phase, and this endotherm shifted to higher temperature with increasing iodine content. All the $[\text{NP}(\text{OTFE})_2]_x\text{I}$ complexes were, therefore, crystalline at ambient temperature. The DSC results for " $[\text{NP}(\text{Cl}_2)]_5\text{I}$ " do not differ significantly from those for $[\text{NP}(\text{Cl}_2)]_n$.

AC impedance data obtained for polyphosphazene-iodine complexes typically display two semi-circles in a Cole-Cole plot indicating two processes with widely separated R-C response. Similar results were obtained previously in studies of both MEEP-polyiodide³ and PPO-polyiodide⁴ complexes. The application of both ac and dc methods and observations on samples of different thickness indicated that the high frequency arc corresponds to a bulk conduction process, while the arc at low frequencies corresponds to an interfacial process. Thus the bulk conductivity of the polyphosphazene-iodine complexes was obtained from the resistance associated with the high-frequency process

and the known cell geometric factor. Arrhenius-type plots are presented (Fig. 2) as well as bulk conductivities at 30°C for all the complexes prepared (Fig. 3).

^{31}P NMR spectra for $[\text{N}(\text{PCl}_2)_2]_n$, $[\text{N}(\text{PCl}_2)_5]\text{I}$, $[\text{NP}(\text{OPr})_2]_n$, $[\text{NP}(\text{OPr})_2]_2\text{I}$, $[\text{NP}(\text{OTFE})_2]_n$, $[\text{NP}(\text{OTFE})_2]_2\text{I}$, MEEP, and MEEP_2I show no significant chemical shift differences between the parent polymers before and after the addition of iodine, and this indicates no covalent bond formation or cleavage of the polyphosphazenes. Similarly, the ^{13}C spectra for $[\text{NP}(\text{OPr})_2]_n$, $[\text{NP}(\text{OPr})_2]_2\text{I}$, $[\text{NP}(\text{OTFE})_2]_n$, $[\text{NP}(\text{OTFE})_2]_2\text{I}$, MEEP and MEEP_2I show no significant chemical shift differences before and after the addition of iodine.

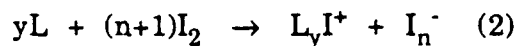
Discussion

The brown-black color and characteristic Raman bands demonstrate clearly the presence of polyiodide anions, I_n^- , in the MEEP_xI , $[\text{NP}(\text{OTFE})_2]_x\text{I}$, and $[\text{NP}(\text{OPr})_2]_x\text{I}$ complexes. No Raman bands corresponding to molecular I_2 appeared for MEEP_xI and $[\text{NP}(\text{OPr})_2]_x\text{I}$, and these samples do not readily evolve iodine. This suggests that iodine is not incorporated in the molecular form I_2 . $[\text{NP}(\text{OTFE})_2]_x\text{I}$ complexes did sometimes show I_2 (vapor) bands in the Raman, along with a loss of coloration, which suggest only weak complex formation. The purple color in the $[\text{N}(\text{PCl}_2)_2]_x\text{I}$ complexes suggested that molecular I_2 is present in the polymer. Although the instability of the complex precluded direct detection of I_2 by Raman spectroscopy, further indirect evidence for simple I_2 incorporation includes (1) the facile evolution of I_2 , (2) the relatively low degree of iodine incorporation, and (3) the unchanged morphology and thermal properties of the polymer following incorporation of the iodine.

Since polyiodide formation involves the reduction of I_2 , a compensating oxidative

half-reaction must also occur. No oxidation products in the complexes could be detected by NMR methods, and this suggests that in each case the polyphosphazenes remain intact. Apparently, the polymer backbone and side chains are not chemically altered by iodine uptake. DSC traces of the complexes, which show increasing T_g with increasing iodine loading and no new thermal features, also indicate that the polymers do not undergo structural degradation. Oxidation involving the formation of a delocalized positive charge along the polymer backbone (such as is found in conjugated backbone polymers)⁶ seems unlikely in the case of polyphosphazenes, which do not possess the extensive electron delocalization characteristic of conjugated carbon chains.²² The electrochemical stability of MEEP²³ indicates that the polymer should not be oxidized by I_2 . This leads us to conclude that the compensating half-reaction is the oxidation of I_2 .

The stabilization of iodonium via a complexation equilibrium:



has been suggested³ previously as a redox disproportionation process that may lead to the formation of polyiodides in MEEP_xI complexes. Direct evidence for the existence of an iodonium complex is presently lacking. Poly(propylene) oxide (PPO) will stabilize polyiodide, yet small-molecule ethers such as diethyl ether and diglyme do not bring about redox disproportionation of iodine.⁴ Thus, it is unclear whether the oligo-ether side groups in MEEP can act as stabilizing ligands for the iodonium cation. The compounds [NP(OTFE)₂] and [NP(OPr)₂] contain only a single oxygen atom in each side-chain which is sterically restricted and reduced in basicity by bonding to phosphorus.

The conductivities of MEEP_xI and [NP(OPr)₂]_xI were examined well above the T_g

and show a temperature dependence that is close to Arrhenius-type $\exp(1/T)$ response, (Fig. 2). The bulk conductivity data do not show a VTF-type correlation²⁴ with T_g , as both T_g and conductivities increase with increasing iodine content. For these reasons, effects other than local polymer dynamics (for example, carrier number or type) may dominate the conduction process. It is also interesting to note that despite an increase in T_g , the MEEP_xI and $[\text{NP}(\text{OPr})_2]_x\text{I}$ complexes become markedly less viscous with increased iodine loading; similar observations were made for MEEP_xMI_n complexes.³

Bulk conductivities as a function of iodine content are given in Fig. 3. MEEP_xI and $[\text{NP}(\text{OPr})_2]_x\text{I}$ show similar behavior, which involves a marked increase in conductivity even at low iodine loadings ($x = 16$) and a more gradual increase with higher iodine loading. The $[\text{NP}(\text{Cl}_2)]_x\text{I}$ complexes show no enhancement in conductivity compared with the pristine polymer (approx. 10^{-8} Scm^{-1}). $[\text{NP}(\text{OTFE})_2]_x\text{I}$ complexes show only a very slight increase in conductivity over that of the parent polymer. $[\text{NP}(\text{Cl}_2)]_x\text{I}$ complexes do not contain polyiodides, and $[\text{NP}(\text{OTFE})_2]_x\text{I}$ complexes are crystalline at ambient temperature. Therefore, neither exhibits high conductivity. Further illustrations of this behavior can be found in both PPO_xMI_n and MEEP_xMI_n complexes, in which the amorphous complexes which contain I_n^- are highly conducting.

The mode of conduction within polymer-polyiodide complexes has been addressed previously.^{3,4} Impedance measurements for all the polymer-polyiodide complexes studied in these laboratories consistently show that both interfacial and bulk conduction processes are present. In summary, the present research on the interaction of I_2 with a diverse set of polymers indicates that the conduction process involves the polyiodides rather than the polymer backbone, and that polyether sidechains are conducive to polyiodide formation.

Acknowledgements. The research at Northwestern University was supported by DOE by grant DE-FG02-85ER45220 and the facilities were provided by the Northwestern Materials Research Center sponsored by the National Science Foundation Grant No. DMR 881571. The research at The Pennsylvania State University was supported by the Office of Naval Research. M.L. acknowledges support by the National Science Foundation under grant CHE-8807987 awarded in 1988.

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Table 1. Reaction products obtained by the interaction of polyphosphazenes with iodine.

<u>compound</u>	<u>color</u>	<u>morphology</u>
$[\text{NP}(\text{OTFE})_2]_n$	white	soft solid
$[\text{NP}(\text{OTFE})_2]_{16}\text{I}$	brown	fibrous
$[\text{NP}(\text{OTFE})_2]_4\text{I}$	brown	fibrous
$[\text{NP}(\text{OTFE})_2]_2\text{I}$	brown	fibrous
$[\text{NP}(\text{OPr})_2]_n$	light brown	elastomeric
$[\text{NP}(\text{OPr})_2]_{16}\text{I}$	brown-black	tacky liquid
$[\text{NP}(\text{OPr})_2]_4\text{I}$	brown-black	tacky liquid
$[\text{NP}(\text{OPr})_2]_2\text{I}$	brown-black	tacky liquid
$[\text{NPCL}_2]_n^{\text{a}}$	white-colorless	elastomeric
$[\text{NPCL}_2]_{16}\text{I}$	purple	elastomeric
$[\text{NPCL}_2]_5\text{I}^{\text{b}}$	purple	elastomeric
MEEP	light brown	tacky viscous liquid
$\text{MEEP}_{1.3}\text{I}$	brown-black	tacky liquid
$\text{MEEP}_{0.7}\text{I}$	brown-black	tacky liquid
$\text{MEEP}_{0.4}\text{I}$	brown-black	tacky liquid

^a Sometimes has a yellow or brown tinge.

^b Solid I_2 remained even after several days of reaction when a loading of iodine at $\text{I}:\text{PN}::1:5$ or higher was attempted. The actual iodine loading is therefore less than indicated by the formula.

Table 2. Resonance Raman data for polyphosphazene-iodine complexes.

<u>compound</u>	<u>peak Position (cm⁻¹)^a</u>	<u>relative intensity</u>
MEEP _{1.3} I	113	34
	174	100
MEEP _{0.7} I	109	34
	172	100
MEEP _{0.4} I	113	41
	178	100
[NP(OPr) ₂] ₁₆ I	110	66
	164	100
[NP(OPr) ₂] ₄ I ^b	110	41
	168	100
[NP(OPr) ₂] ₂ I	100	62
	167	100
[NP(OTFE) ₂] ₂ I ^b	112	73
	169	100

^a There is a shoulder or small peak at ca. 145 cm⁻¹ in every spectrum.

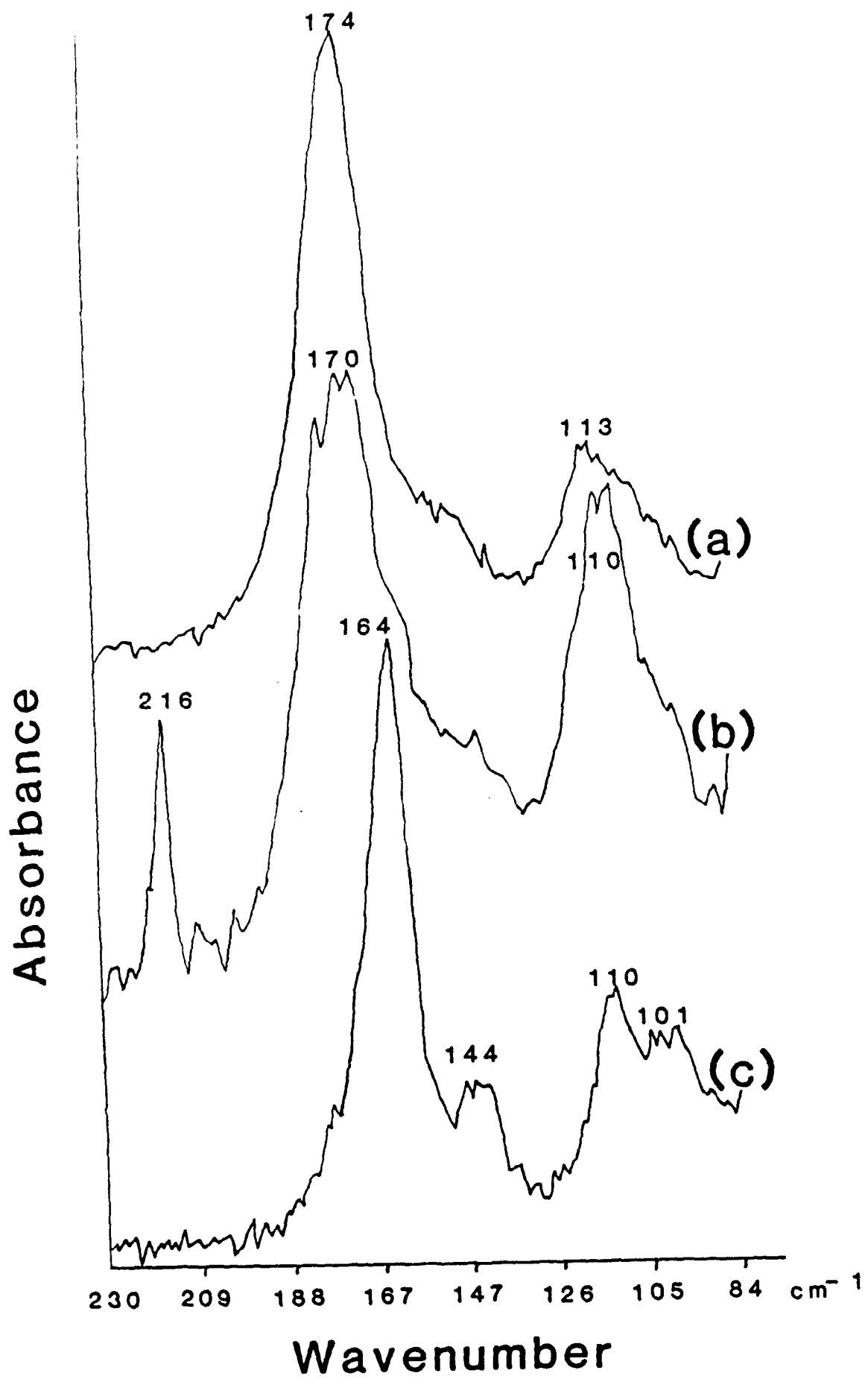
^b There is a small peak at 217 cm⁻¹ due to I₂ vapor.

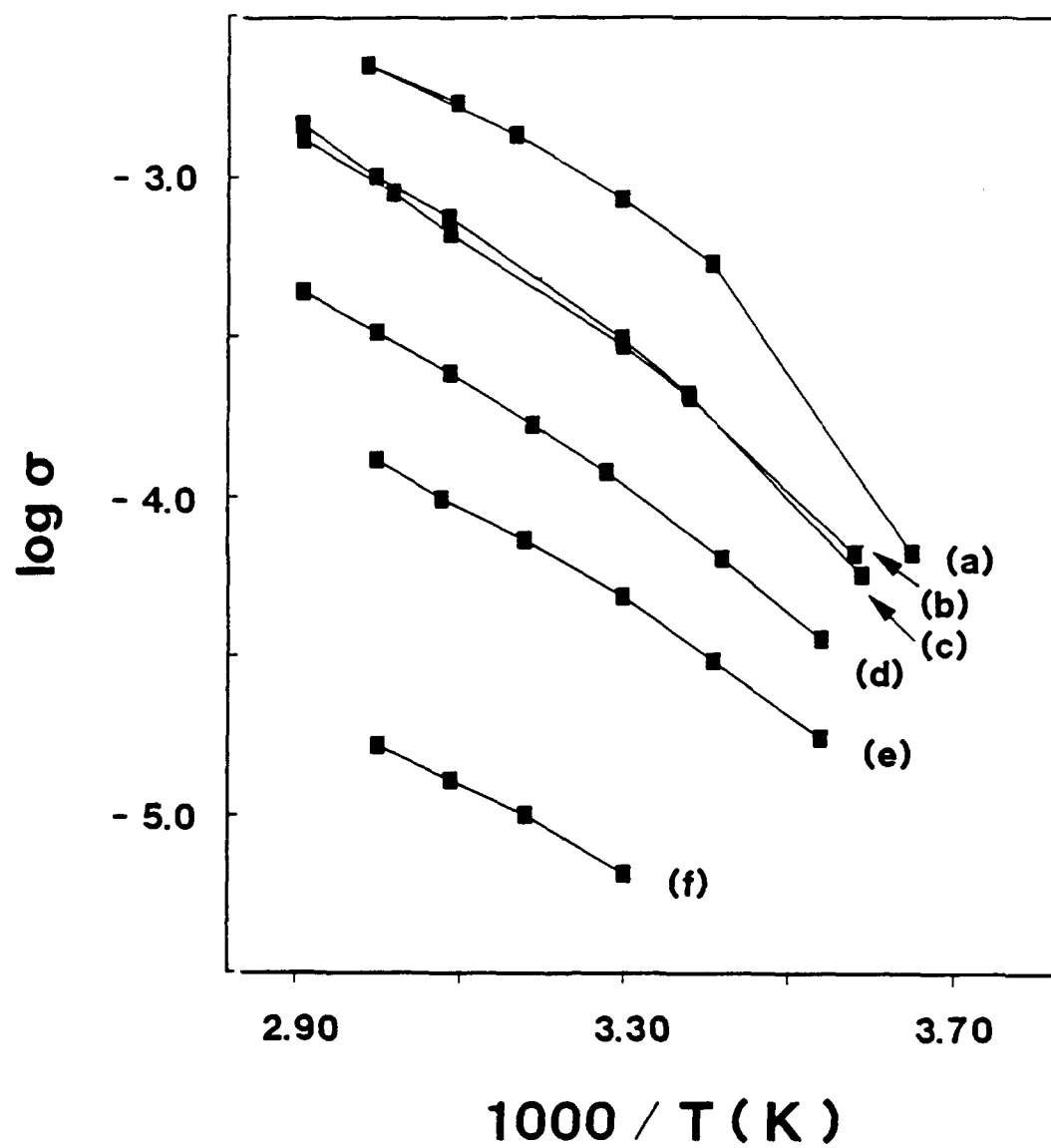
Table 3. Glass transition temperatures and melting points for polyphosphazene-iodine complexes.

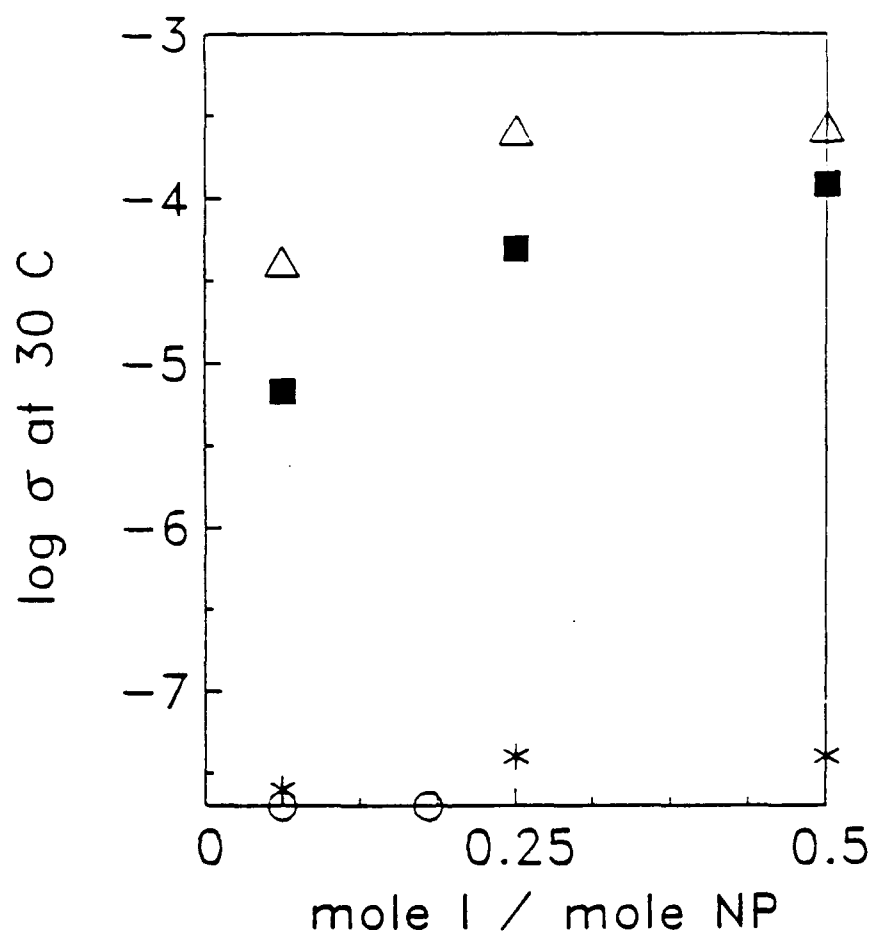
<u>compound</u>	<u>T_g / K</u>	<u>compound</u>	<u>T_m / K</u>
MEEP	193	NP(OTFE) ₂	311
MEEP _{1.3} I	211	[NP(OTFE) ₂] ₁₆ I	305
MEEP _{0.7} I	215	[NP(OTFE) ₂] ₄ I	317
MEEP _{0.4} I	226	[NP(OTFE) ₂] ₂ I	319
[NP(OPr) ₂] _n	170		
[NP(OPr) ₂] ₁₆ I	169		
[NP(OPr) ₂] ₄ I	181		
[NP(OPr) ₂] ₂ I	189		
[PNCl ₂] _n	204		
[PNCl ₂] ₂ I	206		

Figure Captions:

- Figure 1. Raman spectra for (a) $\text{MEEP}_{1.3}\text{I}$, (b) $[\text{NP}(\text{OTFE})_2]_2\text{I}$ and (c) $[\text{NP}(\text{OPr})_2]_{16}\text{I}$. Peak positions are indicated on spectra.
- Figure 2. $\log \sigma$ vs. $1000/T$ for (a) $\text{MEEP}_{0.4}\text{I}$, (b) $\text{MEEP}_{0.7}\text{I}$, (c) $\text{MEEP}_{1.3}\text{I}$, (d) $[\text{NP}(\text{OPr})_2]_2\text{I}$, (e) $[\text{NP}(\text{OPr})_2]_4\text{I}$, and (f) $[\text{NP}(\text{OF})_2]_{16}\text{I}$.
- Figure 3. Conductivity in polyphosphazene-iodine complexes as a function of iodine concentration. Δ $\text{R}=\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, \blacksquare $\text{R}=\text{OCH}_2\text{OCH}_2\text{CH}_3$, * $\text{R}=\text{OCH}_2\text{CF}_3$, \circ $\text{R}=\text{Cl}$.







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